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Total Pages: ~~30~~ 33

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ENTRANCE EXAMINATION, 2012

**Pre-Ph.D./Ph.D.
CHEMICAL SCIENCES**

[Field of Study Code : CHEP (162)]

Time Allowed : 3 hours

Maximum Marks : 75

Weighted : 70

INSTRUCTIONS FOR CANDIDATES

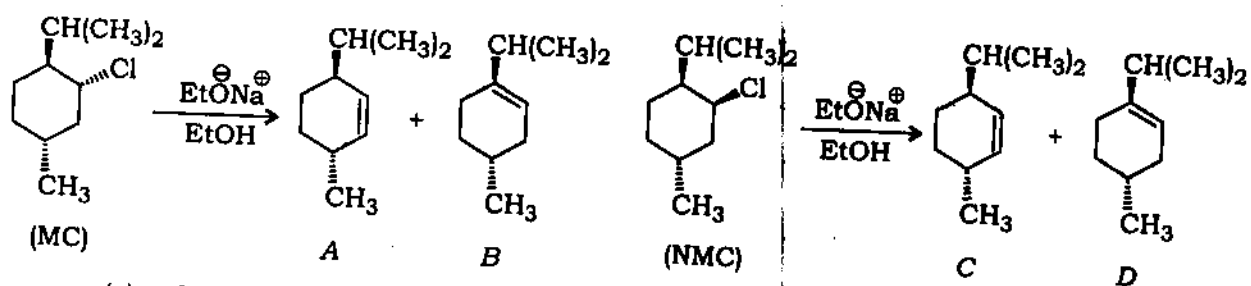
- (i) All questions are compulsory.
- (ii) Answers should be written in the box given in **page 3**.
- (iii) Each correct answer carries 3 marks. Wrong answers carry (-1) mark.
- (iv) Rough work should be done in the space given below the questions.
- (v) If additional space is required, three extra sheets provided at the end of the paper can be utilized for rough work.
- (vi) Use of calculator is permitted.

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Fundamental Constants	Values
Speed of light (c)	$2.99792558 \times 10^8 \text{ m s}^{-1}$
Elementary charge (e)	$1.602176 \times 10^{-19} \text{ C}$
Faraday's constant ($F = N_A e$)	$9.64853 \times 10^4 \text{ C mol}^{-1}$
Boltzmann's constant (k)	$1.38065 \times 10^{-23} \text{ JK}^{-1}$
Gas constant ($R = N_A k$)	$8.31447 \text{ JK}^{-1} \text{ mol}^{-1}$
Planck's constant (h)	$6.62608 \times 10^{-34} \text{ J-s}$
Avogadro's constant (N_A)	$6.02214 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit (u)	$1.66054 \times 10^{-27} \text{ kg}$
Electron mass (m_e)	$9.10938 \times 10^{-31} \text{ kg}$
Electron charge (e)	$4.8 \times 10^{-10} \text{ esu}$
Proton mass (m_p)	$1.67262 \times 10^{-27} \text{ kg}$
Neutron mass (m_n)	$1.67493 \times 10^{-27} \text{ kg}$
Vacuum permittivity ($\epsilon_0 = 1/c^2 \mu_0$)	$8.85419 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
$4\pi\epsilon_0$	$1.11265 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Vacuum permeability (μ_0)	$4\pi \times 10^{-7} \text{ J-s}^2 \text{ C}^{-2} \text{ m}^{-1}$
Bohr magneton ($\mu_B = e\hbar/2m_e$)	$9.27401 \times 10^{-24} \text{ JT}^{-1}$
Nuclear magneton ($\mu_N = e\hbar/2m_p$)	$5.05078 \times 10^{-27} \text{ JT}^{-1}$
Bohr radius ($a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$)	$5.29177 \times 10^{-11} \text{ m}$
Fine-structure constant ($\alpha = \mu_0 e^2 c / 2\hbar$)	7.29735×10^{-3}
Inverse of fine-structure constant (α^{-1})	1.37036×10^2
Second radiation constant ($c_2 = hc/k$)	$1.43878 \times 10^{-2} \text{ m-K}$
Standard acceleration of free fall (g)	9.80665 m s^{-2}

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1. Menthyl chloride (MC) and neomenthyl chloride (NMC) upon reaction with sodium ethoxide in ethanol would produce the following products, respectively :



- (a) Only B; C (minor) and D (major)
 (b) Only A; C (minor) and D (major)
 (c) A (major), B (minor); C (major) and D (minor)
 (d) A (minor), B (major); only C

2. The basicity of EtNH_2 (I), $\text{HN}=\text{C}(\text{NH}_2)_2$ (II) and $\text{CH}_3\text{C}(\text{NH})\text{NH}_2$ (III) would follow the following order :

- (a) $\text{II} > \text{III} > \text{I}$
 (b) $\text{III} > \text{II} > \text{I}$
 (c) $\text{I} > \text{II} > \text{III}$
 (d) $\text{I} > \text{III} > \text{II}$

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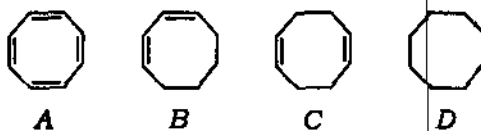
3. The conversions of cyclohexanone oxime to Nylon-6 and cyclic ketones to lactones involve, respectively

- (a) Curtius rearrangement and Wolff rearrangement
- (b) Wolff rearrangement and Lossen rearrangement
- (c) Beckmann rearrangement and Baeyer-Villiger oxidation
- (d) Curtius rearrangement and Baeyer-Villiger oxidation

4. The following is true for Cope reaction :

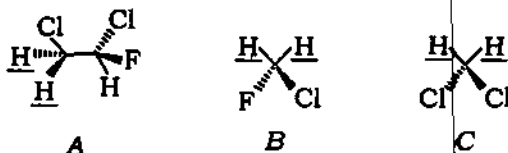
- (a) Occurs at low temperature, tertiary amines are reactants, proceeds through SYN pathway
- (b) Occurs at low temperature, tertiary amine oxides are reactants, proceeds through SYN pathway
- (c) Occurs at high temperature, tertiary amine oxides are reactants, proceeds through ANTI pathway
- (d) Occurs at low temperature, tertiary amine oxides are reactants, proceeds through ANTI pathway

5. Match the structure of the eight-membered ring compounds (A-D) with the following $^1\text{H-NMR}$ chemical shifts (in ppm) :



- (a) A: δ 5.74 (s); B: δ 1.20 – 1.70 (m, 4H), 1.85 – 2.50 (m, 4H), 5.35 – 5.94 (m, 4H); C: δ 2.39 (m, 8H), 5.60 (m, 4H); D: δ 1.54 (s)
- (b) A: δ 1.54 (s); B: δ 2.39 (m, 8H), 5.60 (m, 4H); C: δ 1.20 – 1.70 (m, 4H), 1.85 – 2.50 (m, 4H), 5.35 – 5.94 (m, 4H); D: δ 5.74 (s)
- (c) A: δ 1.54 (s); B: δ 1.20 – 1.70 (m, 4H), 1.85 – 2.50 (m, 4H), 5.35 – 5.94 (m, 4H); C: δ 2.39 (m, 8H), 5.60 (m, 4H); D: δ 5.74 (s)
- (d) A: δ 5.74 (s); B: δ 2.39 (m, 8H), 5.60 (m, 4H); C: δ 1.20 – 1.70 (m, 4H), 1.85 – 2.50 (m, 4H), 5.35 – 5.94 (m, 4H); D: δ 1.54 (s)

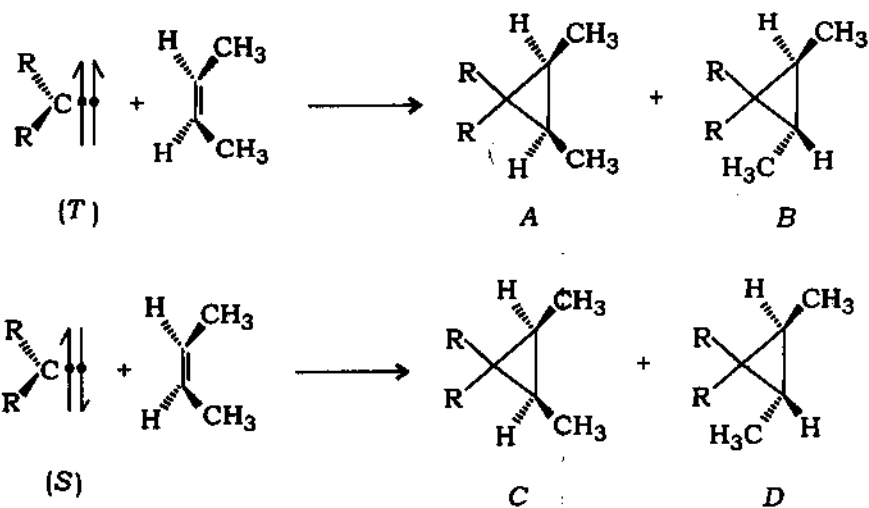
6. The underlined H atoms in molecules A, B and C are, respectively



- (a) Enantiotopic, homotopic and diastereotopic
- (b) Diastereotopic, enantiotopic and homotopic
- (c) Homotopic, enantiotopic and diastereotopic
- (d) Enantiotopic, diastereotopic and homotopic

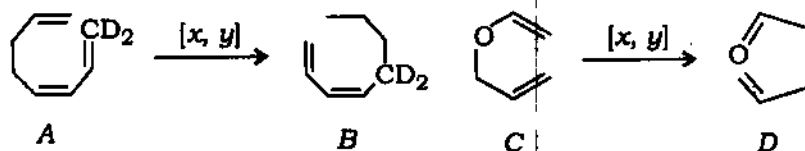
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7. Addition of a triplet (*T*) carbene to an alkene and a singlet (*S*) carbene to an alkene would produce, respectively



- (a) Only A and only D
 (b) Only B and only C
 (c) A and B and only D
 (d) A and B and only C

8. The reactions of A to B and C to D are examples of [*x*, *y*] type of sigmatropic shifts, which can be denoted as



- (a) [1, 8] and [1, 3]
 (b) [3, 5] and [1, 3]
 (c) [3, 5] and [3, 3]
 (d) [1, 8] and [3, 3]

9. The following is true for the complex of [18] crown-6 and KMnO_4 :
- (a) Ion-dipole interaction, phase transfer catalyst, turns benzene purple
 - (b) π - π interaction, acid catalyst, turns benzene purple
 - (c) π - π interaction, phase transfer catalyst, turns benzene yellow
 - (d) Ion-dipole interaction, acid catalyst, turns benzene yellow

10. XeF_2 , $[\text{XeF}_5]^-$, SF_4 , $[\text{BrF}_4]^-$ have the following molecular shapes, respectively :
- (a) Tetrahedral, pentagonal planar, trigonal bipyramid, linear
 - (b) Linear, trigonal bipyramid, pentagonal planar, tetrahedral
 - (c) Trigonal bipyramid, pentagonal planar, tetrahedral, linear
 - (d) Linear, pentagonal planar, trigonal bipyramid, tetrahedral

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11. Symmetry operators that are lost in going from NH_3 to NH_2Cl are

- (a) C_3 and two σ_v
- (b) C_2 and two σ_v
- (c) C_3 and one σ_v
- (d) C_2 and one σ_v

12. How many degrees of vibrational freedom do SiCl_4 , BrF_3 and POCl_3 possess?

- (a) 9, 6 and 9, respectively
- (b) 6, 9 and 6, respectively
- (c) 4, 3 and 4, respectively
- (d) 5, 4 and 5, respectively

13. The number of framework electrons in the closo, nido and arachno series would equal to

- (a) $2n + 2$, $2n + 4$ and $2n + 6$, respectively
- (b) $2n + 6$, $2n + 4$ and $2n + 2$, respectively
- (c) $2n + 4$, $2n + 2$ and $2n + 6$, respectively
- (d) $2n + 6$, $2n + 2$ and $2n + 4$, respectively

14. The spin only magnetic moment, (μ_s) for Co(III) octahedral complex with weak field ligand and Co(II) in a tetrahedral would be

- (a) 3.87 BM and 1.73 BM
- (b) 0 BM and 1.73 BM
- (c) 1.73 BM and 3.87 BM
- (d) 4.90 BM and 3.87 BM

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15. Jahn-Teller distortion would be exhibited by the following :

- (a) Cr(II) and Mn(III) in weak ligand field
- (b) Co(III) and Fe(II) in strong ligand field
- (c) Cr(III) in weak ligand field
- (d) Ni(II) and Fe(III) in weak ligand field

16. Which of the following is a haem iron protein?

- (a) Rubredoxin
- (b) Transferrin
- (c) Haemerythrin
- (d) Cytochrome c

17. The ground state terms for Ti(III) and Mn(II) would, respectively, be

- (a) 3F and 4F
- (b) 2D and 6S
- (c) 4F and 5D
- (d) 2D and 4F

18. In computational chemistry, one calculates the lowest energy structure of molecule through variation principle using Hartree-Fock equation, $F_i \Phi_i = \epsilon \Phi_i$. In this equation, the Fock operator (F_i) is expressed as

- (a) $F_i = h_j + \sum_j (J_j - K_j)$, with $h_j = -(\hbar^2 / 2m_e) \nabla_j^2 - \sum_n (Z_n e / |R_n - r_e|)$, and J as Coulomb operator and K as exchange operator, where i and j are indices for different electrons
- (b) $F_i = h_i + \sum_i (J_i - K_i)$, with $h_i = -(\hbar^2 / 2m_e) \nabla_i^2 - \sum_n (Z_n e / |R_n - r_e|)$, and J as Coulomb operator and K as exchange operator, where i and j are indices for different electrons
- (c) $F_i = h_i + \sum_j (J_j - K_j)$, with $h_i = -(\hbar^2 / 2m_e) \nabla_i^2 - \sum_n (Z_n e / |R_n - r_e|)$, and J as Coulomb operator and K as exchange operator, where i and j are indices for different electrons
- (d) $F_i = h_i + \sum_i (J_i - K_i)$, with $h_i = -(\hbar^2 / 2m_e) \nabla_j^2 - \sum_n (Z_n e / |R_n - r_e|)$, and J as exchange operator and K as Coulomb operator, where i and j are indices for different electrons

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19. If the estimated dipole moment and bond length of HCl are 1.1 D and 1.28 Å, respectively, the percentage ionic character in HCl molecule is

(a) 12.8%

(b) 86.3%

(c) 85.9%

(d) 17.9%

20. Maximum entropy of a mixture of hexane and heptane occur when they are mixed in a proportion of

(a) 86 gm and 100 gm

(b) 86 gm and 1 gm

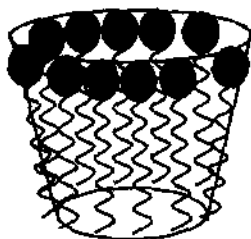
(c) 1 gm and 100 gm

(d) 8.6 gm and 10 gm

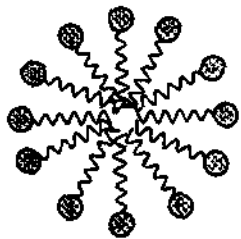
21. If at a given temperature, the equilibrium constant (K) of the reaction $\text{NO (g)} + \frac{1}{2}\text{O}_2 \text{ (g)} \rightleftharpoons \text{NO}_2 \text{ (g)}$ is $(K) = 4 \times 10^{-3}$, then the equilibrium constant (K') for the reaction $2\text{NO}_2 \text{ (g)} \rightleftharpoons 2\text{NO (g)} + \text{O}_2 \text{ (g)}$ is

- (a) 4×10^{-3}
- (b) 16×10^3
- (c) 6.25×10^4
- (d) 1.6×10^{-4}

22. Which of the following pictures is the most appropriate for reverse-micelle structure?



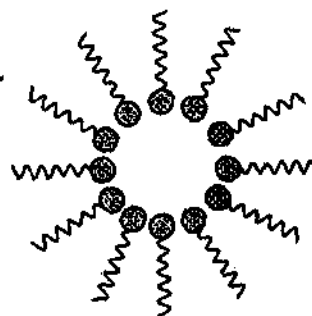
(a)



(b)



(c)



(d)

23. The wave function of a quantum particle is given by $\psi(x) = e^{-ax}$. The expectation value, $\langle x \rangle$ in the range $x = -1$ to 1 is given by

(a) $(1/a) e^{-2a}$

(b) e^{-2a}

(c) $(1/a^2) e^{-2a}$

(d) $(1/a) e^{-a}$

24. A substance, when dissolved in water at $10^{-3} M$ concentration, absorbs 10% of an incident radiation in a path of 1 cm length. In order to absorb 90% of same radiation, the concentration of the solution should be

(a) $21.8 \times 10^{-3} M$

(b) $9.5 \times 10^{-3} M$

(c) $27.4 \times 10^{-3} M$

(d) $18 \times 10^{-3} M$

25. HCl molecule is well described by the Morse potential ($V = hcD_e[1 - e^{-a(R - R_e)}]^2$) with $D_e = 42940.6 \text{ cm}^{-1}$, $\nu = 2990 \text{ cm}^{-1}$ and $x_e \nu = 52 \text{ cm}^{-1}$ (x_e is the anharmonicity constant). The dissociation energy of HCl molecule is

- (a) 39950.6 cm^{-1}
- (b) 41458.6 cm^{-1}
- (c) 42940.6 cm^{-1}
- (d) 40002.6 cm^{-1}

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ENTRANCE EXAMINATION, 2011

**Pre-Ph.D./Ph.D.
CHEMICAL SCIENCES**

[Field of Study Code : CHEP (162)]

Time Allowed : 3 hours

Maximum Marks : 70

INSTRUCTIONS FOR CANDIDATES

- (i) All questions in **Part—A** are compulsory.
- (ii) The answers for **Part—A** must be written in the box provided on **page 3**.
- (iii) Answer *only 8* questions from **Part—B**.
- (iv) Answer for **Part—B** must be done in the space provided along with the question.
- (v) Extra sheets for Rough Work have been provided at the end.
- (vi) Use of calculator is permitted.

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PART—A

I. Answer all the **twenty** (20) multiple-choice questions from this Part :

$1\frac{1}{2} \times 20 = 30$

A1. The entropy change for the reaction $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$ for which $\Delta H^\circ = -1648 \text{ kJ mol}^{-1}$ (Given, molar entropy change for Fe, O_2 and Fe_2O_3 are 27.3, 205.1 and 87.4 JK^{-1} at temperature 298 K) is

- (a) $5980 \text{ JK}^{-1} \text{ mol}^{-1}$
- (b) $-549.5 \text{ JK}^{-1} \text{ mol}^{-1}$
- (c) $4980.7 \text{ JK}^{-1} \text{ mol}^{-1}$
- (d) $-18.85 \text{ JK}^{-1} \text{ mol}^{-1}$

A2. If the rate constants for decomposition $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2}\text{O}_2$ are 3.46×10^{-5} and 4.87×10^{-3} at 25°C and 65°C respectively (Given, $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$), then the activation energy is given by

- (a) $26.8 \text{ kcal mol}^{-1}$
- (b) $24.8 \text{ kcal mol}^{-1}$
- (c) $23.5 \text{ kcal mol}^{-1}$
- (d) $48.2 \text{ kcal mol}^{-1}$

A3. The quantum number of the Bohr orbit in a hydrogen atom whose radius is 0.01 mm (Given, the Bohr radius of hydrogen atom is $5.292 \times 10^{-11} \text{ m}$), is

- (a) 5
- (b) 189225
- (c) 435
- (d) Cannot be calculated

A4. In the context of self-assembled Micellar structure, which statement is true?

- (a) Micelles can be formed by self-assembling surfactant molecules in any polar solvent except water.
- (b) Micelles can only be formed above a particular concentration of surfactant known as Critical Association Concentration.
- (c) Micelles can only form above a critical temperature known as Krafft temperature.
- (d) In a Micellar structure, hydrophobic surface and hydrophilic core can be formed.

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A5. The normalized mean value of x for a probability distribution function $f(x)$ can be obtained by

$$(a) \langle x \rangle = \frac{\int_{-\infty}^{\infty} (f(x))^2 dx}{\int_{-\infty}^{\infty} f(x) dx}$$

$$(b) \langle x \rangle = \frac{\int_{-\infty}^{\infty} x (f(x))^2 dx}{\int_{-\infty}^{\infty} f(x) dx}$$

$$(c) \langle x \rangle = \frac{\int_{-\infty}^{\infty} x f(x) dx}{\int_{-\infty}^{\infty} f(x) dx}$$

$$(d) \langle x \rangle = \frac{\left\langle \int_{-\infty}^{\infty} x^2 f(x) dx \right\rangle}{\int_{-\infty}^{\infty} f(x) dx}$$

A6. For a simple diatomic molecule, the functional form of the potential energy curve can be expressed (with usual terms) as

$$(a) V(r) = D_e [1 + e^{-a(r-r_e)^2}]$$

$$(b) V(r) = D_e [1 - e^{-a(r-r_e)^2}]$$

$$(c) V(r) = -D_e [e^{-a(r-r_e)^2} - 1]$$

$$(d) V(r) = D_e [1 - e^{a(r-r_e)^2}]$$

A7. A dye solution of concentration $26 \mu M$ shows the optical density of 0.5 in a 1 cm quartz cell at 400 nm. The molar extinction coefficient of the dye is given by

$$(a) 192307.7 M^{-1} \text{ mm}^{-1}$$

$$(b) 52 M^{-1} \text{ cm}^{-1}$$

$$(c) 13000 M^{-1} \text{ mm}^{-1}$$

(d) Cannot be calculated

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A8. S_N1 reaction of $R-X$ with $AgCN$ and S_N2 reaction of $R-X$ with $NaCN$ would produce

- (a) $R-N\equiv C$ and $R-C\equiv N$
- (b) $R-C\equiv N$ and $R-C\equiv N$
- (c) $R-C\equiv N$ and $R-N\equiv C$
- (d) $R-N\equiv C$ and $R-N\equiv C$

A9. OsO_4 and peroxyacids would promote stereoselective hydroxylation of alkenes

- (a) in SYN and ANTI manner, respectively
- (b) both in SYN manner
- (c) both in ANTI manner
- (d) in ANTI and SYN manner, respectively

A10. Suzuki cross-coupling reaction involves

- (a) organoboronic acid, alkyl or aromatic halide, Pd catalyst and an acid
- (b) organoboronic acid, alkyl or aromatic halide, Pd catalyst and base
- (c) organoboronic acid and alkyl or aromatic halide
- (d) organoboronic acid, alkyl or aromatic halide, Pd catalyst

A11. X_2CHCF_3 ($X = \text{Halide}$) in presence of base leads to the formation of $X_2C=CF_2$ following the mechanism

- (a) S_N1
- (b) E1
- (c) E2
- (d) E1cB

[P.T.O.]

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A12. Which of the following is true for Cope rearrangement?

- (a) [1,5] shift, intramolecular, uncatalyzed
- (b) [3,3] shift, intramolecular, uncatalyzed
- (c) [3,3] shift, intramolecular, catalyzed
- (d) [1,5] shift, intermolecular, catalyzed

A13. An examination of saturated hydrocarbons containing methyl groups show asymmetrical (ν_{as}) and symmetrical (ν_s) stretching modes in the region of

- (a) 2960 and 2870 cm^{-1}
- (b) 3200 and 3100 cm^{-1}
- (c) 1800–1700 cm^{-1}
- (d) 1650–1450 cm^{-1}

A14. $^1\text{H-NMR}$ spectra of $(\text{CH}_3)_2\text{O}$, CH_3F and RCOOH show chemical shift (δ) in ppm at

- (a) 3.27, 4.30 and 10.8, respectively
- (b) 4.30, 3.27 and 10.8, respectively
- (c) 3.27, 10.8 and 4.30, respectively
- (d) 10.8, 4.30 and 3.27, respectively

15. SF_4 has the following geometry

- (a) Octahedral
- (b) Trigonal bipyramidal with lone pair in the axial position
- (c) Trigonal bipyramidal with lone pair in the equatorial position
- (d) Tetrahedral

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A16. NO_2^- and NO_2^+ have the following structure

- (a) Trigonal and linear, respectively
- (b) Both trigonal
- (c) Both linear
- (d) Linear and trigonal, respectively

A17. $d_\pi-d_\pi$ and $d_\pi-\pi^*$ types of donation of electrons from ligand-to-metal is shown by

- (a) alkanes and halides
- (b) R_3P and CN^-
- (c) halides and CN^-
- (d) CN^- and R_3P

A18. The electronic transition of the metal complexes $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ would be

- (a) spin forbidden, Laporte forbidden and spin allowed and Laporte allowed, respectively
- (b) both spin forbidden and Laporte forbidden
- (c) both spin allowed and Laporte allowed
- (d) both spin allowed and Laporte forbidden

A19. μ (calculated) for Cr^{2+} in high-spin and low-spin complexes should be

- (a) 4.90 BM and 2.83 BM, respectively
- (b) 4.90 BM for both
- (c) 1.73 BM and 2.83 BM, respectively
- (d) 4.90 BM and 1.73 BM, respectively

A20. The two-coupled photosynthetic systems PS I and PS II primarily produce

- (a) reduced carbon, ATP and O_2 , respectively
- (b) only ATP
- (c) only reduced carbon
- (d) ATP and reduced carbon, respectively

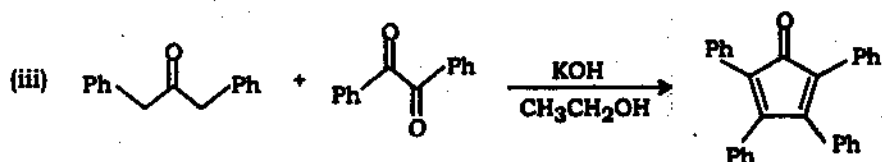
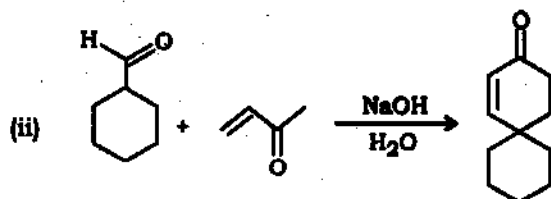
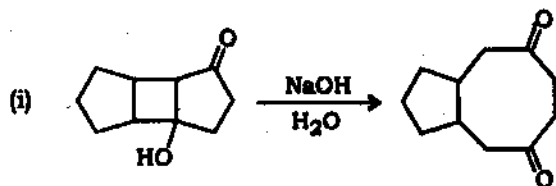
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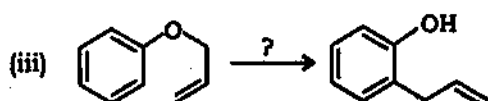
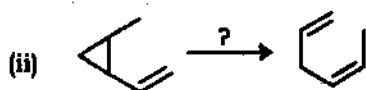
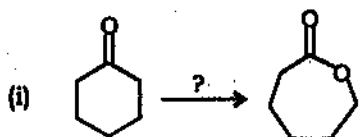
PART-B

1. Answer any eight (8) of the following descriptive questions from this Part : 5×8=40

B1. Write arrow formalism mechanisms for the following reactions (any two) :



B2. Write arrow formalism mechanisms and the conditions for the formation of the following products (any two) :



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B3. Explain with mechanism and energy-profile diagram :

- (a) E2 reaction
- (b) E1 reaction
- (c) E1cB

With an energy-profile diagram, also explain Hammond postulate.

B4. (a) Three bottles containing *o*-dichlorobenzene, *m*-dichlorobenzene and *p*-difluorobenzene are given along with broad-band decoupled ^{13}C -NMR spectra of the three isomers. Assign the three spectra and explain with reasoning :

- (i) δ 127.0, 128.9, 130.6, 135.1 ppm
- (ii) δ 127.7, 130.5, 132.6 ppm
- (iii) δ 116.5, 159.1 ppm

(b) Explain with mechanism :

- (i) Robinson annulation
- (ii) Pinacol-Pinacolone rearrangement

B5. Explain the formation of acetaldehyde from ethylene applying Wacker process.

B6. (a) Reduction of Co(III) in $[\text{Co}(\text{NH}_3)\text{Cl}]^{2+}$ complex by Cr(II) in $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is 10^{10} times faster than the reduction of $[\text{Co}(\text{NH}_3)_6]^{3+}$. Explain in detail.

(b) Permanganate solutions are intrinsically unstable in acidic solutions and decomposition is catalyzed by sunlight. Comment with detailed equations.

B7. Compare the relative O_2 uptake ability of myoglobin and hemoglobin. Describe the cooperativity shown by the heme groups and Bohr effect.

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- B8. (a) $K_2[Pt(CN)_4] \cdot 3H_2O$ is colourless and non-conducting, while $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ is coloured and conducting. Explain.
- (b) Explain the role of $cis-[Pt(NH_3)_2(Cl)_2]$ as an anticancer drug for treating malignant tumours.

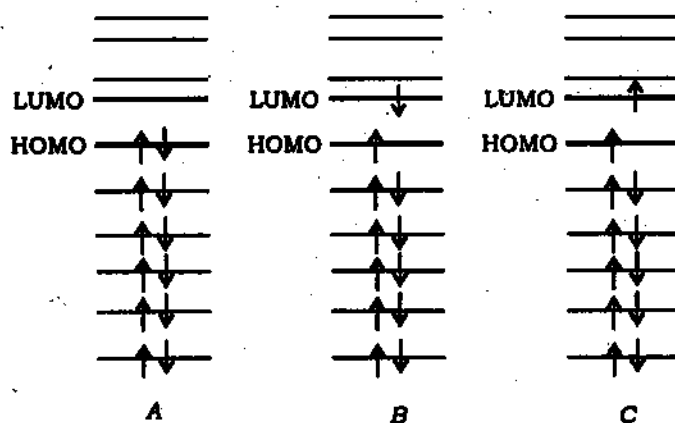
- B9. (a) Starting from the uncertainty principle, $\Delta p \Delta x \geq \frac{\hbar}{2}$, show that for a free particle the uncertainty in energy and time is given by $\Delta E \Delta t \geq \frac{\hbar}{2}$.

- (b) Calculate the wavelength associated with a person of weight 70 kg who walks with a speed of 10 km/h.

- B10. (a) Calculate the percentage ionic character in HCl molecule if the observed dipole moment is 1.08 D and bond length is 1.2746 Å.

- (b) A first-order reflection from the {111} planes of a cubic crystal was observed at a glancing angle of 13.5° when X-rays of wavelength 154 pm were used. Calculate the length of the side of the unit cell.

- B11. (a) Molecular orbital electronic level descriptions of a molecule are shown below :



- Write down the spin multiplicities of the molecule in these three descriptions.
 - Identify the electronic states for the molecule in three descriptions.
 - Explain how the molecule can undergo transitions $A \rightarrow B$, $B \rightarrow C$, $B \rightarrow A$ and $C \rightarrow A$.
 - Arrange the total energy of the molecule in the three descriptions from highest to lowest energy value.
- (b) Explain what is meant by Oscillator Strength of any electronic transition.

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- B12.** (a) With Grotthuss mechanism, explain why molar conductance of H^+ in water is abnormally high.
- (b) What happens to the conductance of electrolytic solutions and of metals with the increase in temperature and why?
- (c) What is the pH of a buffer solution containing 0.2 M hydrofluoric acid (pK_a is 3.2) and 1 M sodium fluoride? What will be the final pH if this buffer is half-diluted?

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Total Pages: 22

ENTRANCE EXAMINATION, 2010

**Pre-Ph.D./Ph.D.
CHEMICAL SCIENCES**

[Field of Study Code : CHEP (162)]

Time Allowed : 3 hours

Maximum Marks : 70

INSTRUCTIONS FOR CANDIDATES

- (i) All questions in **Part-A** are compulsory.
- (ii) The answers for **Part-A** must be written in the box provided on **page 3**.
- (iii) Answer *only* 8 questions from **Part-B**.
- (iv) Answer for **Part-B** must be done in the space provided along with the question.
- (v) Two extra sheets for Rough Work have been provided at the end.
- (vi) Use of calculator is permitted.

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PART—A

- I. Answer all the **twenty** (20) multiple-choice questions from Part—A. More than one correct answer is possible : 1½×20=30

- A1.** For an enzyme-substrate reaction the Michaelis constant is $0.042 \text{ mol dm}^{-3}$. The rate of this reaction is $2.45 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the substrate concentration is 0.89 mol dm^{-3} . The maximum velocity of this enzymolysis is
- (a) $2.57 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$
 - (b) $2.45 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$
 - (c) infinite
 - (d) $1.31 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$
- A2.** The migration of the colloidal particles under the influence of an electric field is known as
- (a) electrophoresis
 - (b) electroosmosis
 - (c) electrodialysis
 - (d) electrodispersion
- A3.** Equivalent conductivity of 0.07 N solution of a monobasic acid is $15.8 \text{ mho cm}^2 \text{ eq}^{-1}$. If the equivalent conductivity of the acid at infinite dilution is $350 \text{ mho cm}^2 \text{ eq}^{-1}$, then the dissociation constant of the acid is
- (a) infinite
 - (b) 2.988×10^{-4}
 - (c) 2.988×10^{-5}
 - (d) 1.494×10^{-4}
- A4.** When $^{14}\text{N}_2$ (with rotational constant of 1.99 cm^{-1}) is exposed to 340 nm light, then the Stokes and anti-Stokes lines for the molecule in second rotational state can be observed at
- (a) 29412 cm^{-1} and 29410 cm^{-1}
 - (b) 340.3 nm and 339.9 nm
 - (c) 14779.9 cm^{-1} and 58529.9 cm^{-1}
 - (d) 29384 cm^{-1} and 29424 cm^{-1}

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- A5.** The general expression for Lennard-Jones potential for the van der Waals interaction between two particles, separated at a distance R , is given by

(a) $V_{LJ} = 4\epsilon \left[\left(\frac{R}{R_0} \right)^{12} - \left(\frac{R}{R_0} \right)^6 \right]$

(b) $V_{LJ} = 4\epsilon \left[\left(\frac{R_0}{R} \right)^{12} - \left(\frac{R_0}{R} \right)^6 \right]$

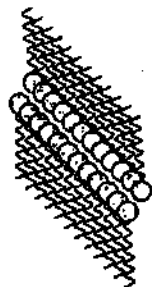
(c) $V_{LJ} = 4\epsilon \left[\left(\frac{R_0}{R} \right)^{12} - \left(\frac{R_0}{R} \right)^{-6} \right]$

(d) $V_{LJ} = 4\epsilon \left[\left(\frac{R_0}{R} \right)^{12} - \left(\frac{R_0}{R} \right)^6 + \epsilon \right]$

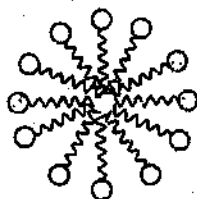
- A6.** Which of the following statements is/are true for Born-Oppenheimer approximation for a molecular system?

- (a) Electronic wavefunctions can be added with nuclear wavefunctions when calculating the ground state energy of the molecule
- (b) Electron motions can be neglected with respect to the nuclear motion when calculating the energy of the molecule
- (c) Electronic and nuclear wavefunctions can be separated because nucleus remains almost stationary during the electron motion in the molecule
- (d) Electronic wavefunction acts in such a way in a molecular system that it provides the potential energy surface (PES) upon which the nuclei move

- A7.** Which of the following pictures is/are the most appropriate for reverse-micelle structure?



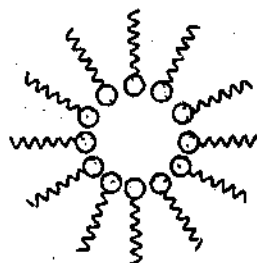
(a)



(b)



(c)



(d)

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A8. The reaction of $\begin{array}{c} \text{Me} \quad \text{Me} \\ | \quad | \\ \text{Me}-\text{C}-\text{C}-\text{Me} \\ | \quad | \\ \text{HO} \quad \text{Br} \end{array}$ with an Ag(I) salt produces

- (a) $\text{Me}_2\text{C}=\text{CMe}_2$
- (b) $\text{Me}_2\text{C(OH)}-\text{C(OH)Me}_2$
- (c) $\text{Me}_3\text{C}-\text{COMe}$
- (d) $\text{Me}_3\text{C}-\text{C(OH)Me}$

A9. The conversion of cyclohexanone oxime to Nylon-6 involves

- (a) Curtius rearrangement
- (b) Schmidt rearrangement
- (c) Beckmann rearrangement
- (d) Baeyer-Villiger oxidation

A10. Perkin reaction involves the following starting material (S) and product (P)

- (a) Aromatic aldehyde (S), acid anhydride (S) and α, β -unsaturated acids (P)
- (b) Aliphatic aldehyde (S), acid anhydride (S) and α, β -unsaturated acids (P)
- (c) Aromatic aldehyde (S), acid (S) and α, β -unsaturated aldehydes (P)
- (d) Aromatic aldehyde (S) and α, β -unsaturated acids (P)

A11. The following is true for Cope reaction

- (a) Occurs at low temp., tertiary amines are reactants, proceeds through SYN pathway
- (b) Occurs at low temp., tertiary amine oxides are reactants, proceeds through SYN pathway
- (c) Occurs at high temp., tertiary amine oxides are reactants, proceeds through ANTI pathway
- (d) Occurs at low temp., tertiary amine oxides are reactants, proceeds through ANTI pathway

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A12. Mass spectrum of butyraldehyde (at 70 eV) due to rearrangement produces a base peak at m/z

- (a) 38
- (b) 48
- (c) 44
- (d) 52

A13. $^1\text{H-NMR}$ chemical shift of CH_3F , CH_3Cl , CH_3Br and CH_3I are

- (a) 2.16, 2.68, 3.05, 4.26
- (b) 4.26, 3.05, 2.16, 2.68
- (c) 4.26, 3.05, 2.68, 2.16
- (d) 2.16, 3.05, 2.68, 4.26

A14. The pK_a of CF_3H (1), C_6H_6 (2), CH_3NO_2 (3), CH_3COCH_3 (4) and CH(CN)_3 (5) would be in the following order

- (a) $2 > 1 > 4 > 3 > 5$
- (b) $1 > 2 > 3 > 4 > 5$
- (c) $3 > 1 > 4 > 2 > 5$
- (d) $5 > 1 > 4 > 3 > 2$

A15. The structures of PCl_5 and I_3^- are

- (a) octahedral and planar triangle
- (b) trigonal bipyramidal and planar triangle
- (c) both trigonal bipyramidal
- (d) octahedral and square planar

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A16. Inert pair effect has been observed in

- (a) Tl(I) and Bi(III)
- (b) Ga(I) and Al(III)
- (c) Ga(I) and In(I)
- (d) B(III) and In(I)

A17. Which of the following is not true for XeF_6 ?

- (a) Produces XeOF_4 with glass
- (b) Distorted octahedron in geometry
- (c) A fluoride donor and an acceptor
- (d) Does not react with water

A18. Applying the Wade's rule, the structures of $\text{B}_{10}\text{C}_2\text{H}_{12}$ and $[\text{B}_9\text{C}_2\text{H}_{11}]^{2-}$, respectively are

- (a) closo and arachno
- (b) nido and closo
- (c) closo and nido
- (d) nido and arachno

A19. Which of the following lanthanide ions is paramagnetic?

- (a) La(III)
- (b) Ce(IV)
- (c) Lu(III)
- (d) Gd(III)

A20. Which of the following is a haem iron protein?

- (a) Rubredoxin
- (b) Transferrin
- (c) Haemerythrin
- (d) Cytochrome c

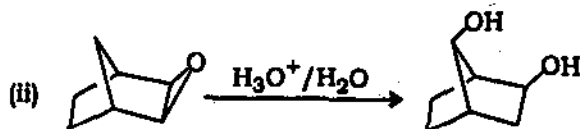
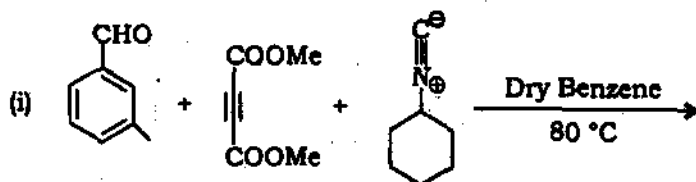
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PART-B

II. Answer any eight (8) descriptive questions from Part-B :

5×8=40

B1. Write the products and arrow formalism mechanisms for the following reactions :



B2. Upon direct photolysis or heating at 220 °C, the dimer of 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (A) yields compound (B). Deduce the structure of compound B using the following spectral data :

Mass m/z = 492; IR(CCl_4) : 1704 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) : 0.73 (s, 3H); 0.92 (s, 3H); 1.51 (s, 3H); 1.88 (s, 3H); 6.6–7.5 (m, 20H).

B3. Explain with mechanism (a) Robinson annulation and (b) Claisen rearrangement.

B4. Explain with specific examples kinetically controlled versus thermodynamically controlled product formation.

B5. Give a detailed account of 'Borazine' describing its structure, synthesis and its properties.

B6. (a) Using Crystal Field Theory, explain why Fe_3O_4 has an inverse spinel structure while Mn_3O_4 has a normal spinel structure.

(b) Explain with examples ligand-to-metal and metal-to-ligand charge transfer in metal complexes.

B7. Describe the functioning of Zn containing enzymes.

B8. Calculate and arrange the following in increasing order of magnetic moment :

(a) CoF_6^{3-}

(b) Co(II) in a tetrahedral

(c) Co(II) in a square planar complex

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- B9.** (a) Explain with a diagram the Nernst diffusion layer for an electrode. Write down the expression for limiting current density for an electrode.
- (b) Estimate the limiting current density at an electrode in solution with Ag^+ concentration of 2.5 mM at 25°C . The thickness of the Nernst diffusion layer is 0.35 mm and the ionic conductivity of Ag^+ at infinite dilution is $6.0 \text{ ms m}^2 \text{ mol}^{-1}$.
- B10.** (a) The rate constant for a certain chemical reaction is $2.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 30°C and $1.38 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 50°C . Evaluate the activation energy of the reaction.
- (b) Consider an electron is moving on a potential curve, $V = (2x^2y + z^3)$. Find the vector field that is acting on that electron at a position $(2, 1, 1)$.
- B11.** State Lambert-Beer law. Derive the expression for absorption in terms of molecular extinction coefficient. A dye solution of concentration $29 \mu\text{M}$ shows the OD of 0.05 in a 0.1 cm quartz cell at an incident wavelength of 400 nm . Calculate the molar extinction coefficient of the dye at that wavelength.
- B12.** (a) What is quantum yield?
- (b) The photodecomposition of HI vapor was carried out with $\lambda = 2070 \text{ \AA}$ radiation. Absorption of each calorie of energy wave gave $1.44 \times 10^{-5} \text{ gram}$ of hydrogen. What is the quantum yield?
- (c) Draw the Jablonski diagram for all possible molecular electronic transitions between three singlet and two triplet states.

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